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## NEW MEASUREMENTS OF THE VAPOR PRESSURE OF MERCURY

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Writing in 1908, Laby<sup>1</sup> remarked "The vapor pressure of mercury is intrinsically important; it has been determined for a wider range of temperatures than that of any other substance. . . . Yet the greatest—and, it should be added, unnecessary—disagreement is to be found in the current values for this vapor pressure, nor is there any table combining all the existing observations." Laby thereupon proceeded to collate the best observations available at that time and published a weighted average table.

In 1910 Smith and I published<sup>2</sup> the results of 43 direct observations of the vapor pressure of mercury by a static method over the temperature range 250° to 435°. The pressure measurement was immensely facilitated by the use of the newly-devised 'static isotenoscope';<sup>3</sup> and a good form of platinum resistance thermometry was available. The average divergence in temperature of an individual observation from the smooth curve given by the equation

$$\log p = 9.9073436 - 3276.628/\theta - 0.6519904 \log \theta, \quad (R)$$

whose constants were chosen to fit our results, was 0.050°. Because of the rather high degree of consistency thus attained, we were encouraged to extrapolate the curve in both directions and found that the values so obtained agreed remarkably well with the average experimental findings of those who had worked either above or below our temperature region.<sup>4</sup> A critical discussion of our own and of the older work on this subject, with tabular comparisons, may be found in the paper referred to.<sup>2</sup>

In 1909, Knudsen developed a relationship<sup>5</sup> connecting the weight of gas passing through tubes containing pierced diaphragms with the difference of gas pressure at the ends, the density of the gas, the resistance of the tube and diaphragm and the time of flow. He applied this to measure the vapor pressure of mercury<sup>6</sup> from 0° to 50°, above which temperature his relationship failed to hold. From the lower to the upper end of this range, his results run from 10.9 to 6.2% respectively in pressure lower than the values given by extrapolation of our 1910 results

by the above equation. This corresponds to temperature discrepancies of  $1^\circ$  at  $0^\circ$  and  $0.8^\circ$  at  $50^\circ$ . One regrets that such an elegant method is not more direct. Later, Knudsen<sup>7</sup> applied his admirable 'absolute manometer,' under certain difficulties, to measure this vapor pressure from  $-10^\circ$  to  $+24.4^\circ$ , and obtained results ranging from about 5% higher to about 10% lower in pressure, at the respective ends of this range, than the values furnished by our equation.

In 1913 Villiers<sup>8</sup> obtained a series of values from  $60^\circ$  to  $100^\circ$  which ran higher than ours by 2.7% of our calculated pressure at  $60^\circ$  to 7.5% at  $100^\circ$ .

In 1914, Haber and Kirschbaum,<sup>9</sup> adopting a suggestion of Langmuir's,<sup>10</sup> measured the damping of a quartz fiber vibrating in mercury vapor at  $20^\circ$ , and obtained a single value by an independent method. This value lies 3.8% in pressure below that given by our equation, or, otherwise, differs by  $0.41^\circ$  for the same pressure.

In glancing over the results obtained by these various workers, here stated baldly without criticism, one is inclined to believe that our equation of 1910 continues to stand the test of time by averaging their scattered results as well as can be hoped for. At the same time one is impressed by the pre-war activity in this field, especially in the lower temperature ranges. It appeared, therefore, to be of interest to obtain, by a method as direct as possible, new measurements below  $250^\circ$ , the lowest point of the range studied in 1910; and, in the work here described I have extended that range from  $250^\circ$  to  $120^\circ$ .

As the static isoteniscope is not especially well suited for the measurement of the rather low pressures with which we are here concerned, an entirely new plan was adopted. Two McLeod gauges of suitable capacities were calibrated and sealed to a central pressure reservoir. The gauges, which were operated by gas pressure and without rubber connections, contained purified mercury. The reservoir and connected gauges could be charged with dry hydrogen at any pressure desired, and sealed off by mercury. The smaller of the two gauges was completely immersed in a riotously stirred oil bath whose temperature was measured by a mercurial thermometer whose thread was all submerged. The corrections of this thermometer were known<sup>11</sup> to tenths of a degree. The other, larger, gauge and the reservoir were maintained in baths at room temperature. On operating the two gauges simultaneously, different pressure readings were obtained, due to the condensation of the mercury vapor that contributed part of the total pressure in the hot gauge; and from this difference in reading the vapor pressure of mercury at the

temperature of the hot gauge could be computed in an obvious manner, if Dalton's law were assumed.

For details of the experiments and mode of reduction of the results, as well as for tabular comparison with the heretofore existing data, a paper may be consulted that will appear elsewhere.<sup>12</sup> It should, however, perhaps be stated here that, at the pressures and compressions used, the neglect of the known divergence of hydrogen from the simple gas laws would cause an error very much smaller than other errors of the experiment. Equilibrium in the hot gauge was, apparently, always established sooner than a measurement could be made. A small correction was applied to correct for the vapor pressure of mercury in the cold gauge. A possible systematic error may arise from the fact that the apparent vapor pressure of a liquid in contact with a gas is not in all cases identical with the vapor pressure at the same temperature of the same liquid in a vacuum. Although this fact was observed by Regnault,<sup>13</sup> it has apparently escaped the notice of many users of the gas-current method for determining small vapor pressures. The error is the greater the more soluble the gas in the liquid, although it is not conditioned solely by this solubility as such. With hydrogen gas at atmospheric pressure, the order of this error,<sup>14</sup> in the case of liquids in which hydrogen shows marked solubility such as ether, carbon disulphide and acetone, is about 1% at 30°; with mercury, in which no evidence of solution was found, and at the temperatures here in question, the order of the error might be expected to be much smaller, were it not that low gas pressures may be especially prejudicial. Further study of this possible error is planned, and one can only say, with T. W. Richards, that these results are of but a preliminary character.

The brief table below summarizes the results obtained. The 'calculated' values in the third column are those derived from the Kirchoff-Rankine-Dupré equation (R), whose constants were given above; the values in the fifth column are likewise derived from this equation. In the last column, *P* stands for the pressure, in millimeters of mercury, of hydrogen in the reservoir.

*Vapor pressures of mercury*

| TEMPERATURE | VAPOR PRESSURE IN MILLIMETERS OF<br>MERCURY AT 0° |       | $\frac{\text{FOUND}}{\text{CALCULATED}} \times 100$ | PERCENTAGE<br>CHANGE OF<br>PRESSURE PER<br>0.1° | <i>P</i> |
|-------------|---|-------|---|---|----------|
|             | Found   | Calc. |   |   |          |
| 191.5°      | 13.02   | 13.02 | 100.00  | 0.34  | 14.28    |
| 150.0°      | 2.802   | 2.811 | 99.67   | 0.39  | 3.564    |
| 121.8°      | 0.829   | 0.823 | 100.75  | 0.47  | 1.738    |

Since the values thus found for the vapor pressures of mercury are obtained, broadly, by subtracting the reading of the smaller and less accurate hot gauge from those of the larger and more accurate cold gauge, it will be seen that the greatest precision (so far as gauge readings are concerned) is to be expected when the vapor pressure most closely<sup>15</sup> approaches  $P$ . This is borne out by the results as tabulated.

It is evident that the results found agree with those calculated almost as closely as can be expected, even having regard to the temperature error ( $0.1^\circ$ ) alone. For this reason one may state, meantime, that the equation (R) may be applied, without alteration of its constants, to give the vapor pressure of mercury over the range  $120^\circ$  to  $250^\circ$  as well as from  $250^\circ$  to  $435^\circ$ , as previously found. A table of the values given by this equation for every two degrees from  $0^\circ$  to  $458^\circ$  has already been published.<sup>2</sup> Further experimental extension of the temperature range, as well as greater precision, may be attempted later, should facilities be available, either by this or else by another method shortly to be described.

It is, perhaps, of interest to consider the upper temperature limit of this vapor pressure curve, namely the critical temperature of mercury. This has been the subject of much speculation.<sup>16</sup> Recently, in 1916 and 1917, J. J. van Laar, employing certain theoretical considerations, has computed  $969^\circ\text{C}$ .<sup>17</sup> and later  $899^\circ\text{C}$ .<sup>18</sup> for the critical temperature; while, in 1918, E. Ariès,<sup>19</sup> from other considerations, arrives at  $1077^\circ\text{C}$ . In such cases, a little experiment is worth much theory. At the Minneapolis meeting of the American Chemical Society in 1910, I described<sup>20</sup> some experiments in which I had heated mercury in a thick-walled capillary tube of quartz glass of 0.2 mm. bore, and continued to see, through a telescope, liquid and gas phases distinct up to  $1275^\circ\text{C}$ . At this temperature the meniscus disappeared; but this was found to be due, not to the attainment of the critical temperature, but to the slight blowing out of the quartz capillary with consequent enlargement of its volume. The tube was never ruptured, but the very viscous liquid quartz glass had yielded somewhat to relieve the rather high pressure of several hundred atmospheres. In 1912, Koenigsberger,<sup>21</sup> using a quartz capillary of dimensions very similar to mine, reported that he had reached the critical temperature about  $1270^\circ\text{C}$ ; but I was able to point out<sup>22</sup> the cause of Koenigsberger's mistake. Owing to lack of facilities, I have not been able to develop this work further; but this has now been done, by the same capillary quartz tube and telescope method, by Bender<sup>23</sup> at Freiburg, who finds that the critical temperature lies between  $1500^\circ$  and  $1600^\circ\text{C}$ .

- <sup>1</sup> Laby, *London, Phil. Mag.*, (Ser. 6), **16**, 1908, (789).
- <sup>2</sup> Smith and Menzies, *J. Amer. Chem. Soc.*, **32**, 1910, (1434).
- <sup>3</sup> Smith and Menzies, *Ibid.*, **32**, 1910, (1412).
- <sup>4</sup> Pfaundler, *Leipzig, Ann. Physik*, (Ser. 3), **63**, 1897, (36); Morley, *Phil. Mag.*, (Ser. 6), **7**, 1904, (662); Hertz, *Ann. Physik*, (Ser. 3), **17**, 1882, (193); Regnault, *Paris, Mém. Acad. Sci.*, **21**, 1847, (30, 502); **26**, 1862, (506); Ramsay and Young, *J. Chem. Soc.*, **49**, 1886, (37); Young, *Ibid.*, **59**, 1891, (629); Cailletet, Colardeau and Rivière, *Paris, C. R. Acad. Sci.*, **130**, 1900, (1585), etc.
- <sup>5</sup> Knudsen, *Ann. Physik*, **28**, 1909, (1002).
- <sup>6</sup> Knudsen, *Ibid.*, **29**, 1909, (184).
- <sup>7</sup> Knudsen, *Ibid.*, **32**, 1910, (809).
- <sup>8</sup> Villiers, *Ann. Chim. Phys.*, (Ser. 8), **30**, 1913, (588).
- <sup>9</sup> Haber and Kirschbaum, *Zr. Elektrochemie*, **20**, 1914, (301).
- <sup>10</sup> Langmuir, *J. Amer. Chem. Soc.*, **35**, 1913, (105).
- <sup>11</sup> Reichsanstalt certificate dated 1914.
- <sup>12</sup> Menzies, *J. Amer. Chem. Soc.*, probably November, 1919.
- <sup>13</sup> Regnault, *Ann. phys. chim.*, (Ser. 3), **15**, 1845, (129); *Mém. Acad. Sci.*, **26**, 1862, (679).
- <sup>14</sup> Campbell, *Trans. Faraday Soc.*, **10**, 1914, (197).
- <sup>15</sup> If these two pressures were very close, and if the gauge tubes were too narrow, the total pressure within the hot gauge might be appreciably greater than the pressure within the reservoir.
- <sup>16</sup> Happel, *Ann. Physik*, (Ser. 4) **13**, 1904, (340), etc.
- <sup>17</sup> Van Laar, *Verslag. Akad. Wetenschappen*, **24**, 1916, (1635).
- <sup>18</sup> Van Laar, *Proc. Acad. Sci. Amsterdam*, **20**, 1917, (138).
- <sup>19</sup> Ariès, *Paris, C. R. Acad. Sci.*, **166**, 1918, (334).
- <sup>20</sup> "A Lower Limit for the Critical Temperature of Mercury," presented before the Division of Inorganic and Physical Chemistry, 1910.
- <sup>21</sup> Koenigsberger, *Chem. Ztg.*, **135**, 1912, (1321).
- <sup>22</sup> Menzies, *J. Amer. Chem. Soc.*, **35**, 1913, (1065).
- <sup>23</sup> Bender, *Physik. Zr.*, **16**, 1915, (246); **19**, 1918, (410).

## COHESION, INTERNAL PRESSURE, ADHESION, TENSILE STRENGTH, TENSILE ENERGY, NEGATIVE SURFACE ENERGY, AND MOLECULAR ATTRACTION

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*Work of adhesion.*—For the past seven years I have been engaged in the study of molecular attraction from a new point of view, as represented by a thermodynamic equation which does not seem to have been developed before, in spite of the fact that it is exceedingly simple. It gives what may be called the *total adhesional energy* ( $E_A$ ), or the total energy involved in the approach of two unlike surfaces. The equation developed by Dupré<sup>1</sup> in 1869 gives the *adhesional work* ( $W_A$ ), which is